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Excess molar enthalpies and excess molar volumes of mixtures of cycloalkanes and pseudo-cycloalkanes

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Abstract

Excess molar enthalpies and volumes were measured at atmospheric pressure and at 298.15 K for three-component systems. A pseudo-cycloalkane of carbon number m was mixed with a cycloalkane of carbon number m over the whole composition range. The values of m ranged from 6 to 8. The results were used to test the principle of congruence.

INTRODUCTION

In an earlier investigation [1], we tested the principle of congruence on a mixture of alkanes and pseudo-alkanes, by means of a novel null method. In this work, a novel set of mixtures involving accurately made up pseudo-cycloalkanes has been used to test the principle which implies that a pseudo-cycloalkane [0.5c-C_kH_{2k} + 0.5c-C_lH_{2l}] will behave like c-C_mH_{2m} where $m = (k + l)/2$. This paper reports H_m^E and V_m^E values for (pseudo-c-C_8H_{16} [0.5c-C_6H_{12} + 0.5-c-$C_{10}H_{20}$] + c-C_8H_{16}), and (pseudo-c-C_7H_{14} [0.5c-C_8H_{16} + 0.5c-C_6H_{12}] + c-C_7H_{14}) and H_m^E values for (pseudo-c-C_6H_{12} [0.5c-C_5H_{10} + 0.5c-C_7H_{14}] + c-C_6H_{12}) and ([0.6c-C_5H_{10} + 0.4c-$C_{10}H_{20}$] + c-C_7H_{14}).

EXPERIMENTAL

The cyclopentane was obtained from Fluka (>99% GC), the cyclohexane from SARchem (99% GC), the cycloheptane from Aldrich (>99% GC), the cyclooctane from Janssen Chemicals (>99% GC), and the

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cyclodecane from Fluka (>99% GC). The pseudo-cycloalkanes were made up as previously described [1]. The H_m^E values were measured using an LKB 2277 (Bioactivity Monitor) microflow calorimeter, and the V_m^E values were measured using an Anton Paar DMA 601 vibrating-tube densimeter. The methods have been previously described [2, 3].

RESULTS

The H_m^E results are given in Table 1, together with the deviations Δ, where

$$\Delta = H_m^E/\text{J mol}^{-1} - x(1-x)\sum_{r=0}^{n} A_r(1-2x)^r$$

The V_m^E values are given in Table 2, together with the deviations Δ′, where

$$\Delta' = V_m^E/\text{cm}^3\,\text{mol}^{-1} - x(1-x)\sum_{r=0}^{n} B_r(1-2x)^r$$

The experimental error in H_m^E is of the order of 1 J mol^{-1} or 1%, and in

TABLE 1

Excess molar enthalpies H_m^E for $x(0.5\text{c-C}_k\text{H}_{2k} + 0.5\text{c-C}_l\text{H}_{2l}) + (1-x)\text{c-C}_m\text{H}_{2m}$ where $m = (k+l)/2$ and for $x(0.6\text{c-C}_5\text{H}_{10} + 0.4\text{c-C}_{10}\text{H}_{20}) + (1-x)\text{c-C}_7\text{H}_{14}$ at 298.15 K

x	H_m^E/ J mol^{-1}	Δ	x	H_m^E/ J mol^{-1}	Δ	x	H_m^E/ J mol^{-1}	Δ
$x(0.5\text{c-C}_5\text{H}_{10} + 0.5\text{c-C}_7\text{H}_{14}) + (1-x)\text{c-C}_6\text{H}_{12}$								
0.1120	9.2	−0.1	0.5609	21.6	0.6	0.8466	10.8	−0.1
0.1638	12.7	0.1	0.6038	20.2	−0.3	0.8787	8.6	−0.2
0.3524	19.6	−0.1	0.7204	17.5	0.1	0.9045	7.3	0.3
0.5408	20.7	−0.4						
$x(0.5\text{c-C}_8\text{H}_{16} + 0.5\text{c-C}_6\text{H}_{12}) + (1-x)\text{c-C}_7\text{H}_{14}$								
0.0648	0.6	0.03	0.4833	2.2	0.04	0.7482	1.6	−0.3
0.1526	1.3	−0.04	0.6222	2.2	−0.4	0.8191	1.3	−0.09
0.1807	1.6	0.03	0.6605	2.9	0.5	0.8287	1.5	0.2
0.2708	2.2	−0.02						
$x(0.5\text{c-C}_{10}\text{H}_{20} + 0.5\text{c-C}_6\text{H}_{12}) + (1-x)\text{c-C}_8\text{H}_{16}$								
0.1676	4.5	−0.4	0.4881	8.6	0.03	0.8168	5.5	−0.04
0.1984	6.1	0.4	0.5638	8.9	−0.2	0.8758	4.2	−0.2
0.3642	8.6	0.0	0.7796	8.3	0.3			
$x(0.6\text{c-C}_5\text{H}_{10} + 0.4\text{c-C}_{10}\text{H}_{20}) + (1-x)\text{c-C}_7\text{H}_{14}$								
0.1625	26.3	0.04	0.4306	47.8	1.5	0.8395	23.1	−0.3
0.2799	39.2	−0.1	0.5307	44.2	−0.9	0.8712	19.8	0.1
0.3991	44.9	−0.8	0.6805	37.8	0.4			

TABLE 2

Excess molar volumes V_m^E for $x(0.5c\text{-}C_kH_{2k} + 0.5c\text{-}C_lH_{2l}) + (1-x)c\text{-}C_mH_{2m}$ where $m = (k+l)/2$ at 298.15 K

x	V_m^E/ $cm^3\ mol^{-1}$	Δ	x	V_m^E/ $cm^3\ mol^{-1}$	Δ	x	V_m^E/ $cm^3\ mol^{-1}$	Δ
$x(0.5c\text{-}C_8H_{16} + 0.5c\text{-}C_6H_{12}) + (1-x)c\text{-}C_7H_{14}$								
0.2191	−0.00203	0.0020	0.4706	−0.00034	0.002	0.7337	−0.00237	0.002
0.3631	−0.00300	−0.001	0.6263	−0.00562	−0.002	0.8569	−0.00488	−0.0006
$x(0.5c\text{-}C_6H_{12} + 0.5c\text{-}C_{10}H_{20}) + (1-x)c\text{-}C_8H_{16}$								
0.0505	−0.00181	−0.003	0.5015	−0.02492	−0.002	0.8135	−0.01438	−0.0004
0.2134	−0.00736	0.003	0.6416	−0.01756	0.002	0.8910	−0.01073	−0.0005
0.3999	−0.02237	−0.0007						

TABLE 3

Coefficients A_r and B_r for H_m^E or V_m^E $[x(0.5c\text{-}C_kH_{2k} + 0.5c\text{-}C_lH_{2l}) + (1-x)c\text{-}C_mH_{2m}]$ where $m = (k+l)/2$ and $[x(0.6c\text{-}C_5H_{10} + 0.4c\text{-}C_{10}H_{20}) + (1-x)c\text{-}C_7H_{14}]$

Mixture	A_0	A_1	A_2
$x(0.5c\text{-}C_5H_{10} + 0.5c\text{-}C_7H_{14}) + (1-x)c\text{-}C_6H_{12}$	85.2145	−0.9939	5.7348
$x(0.5c\text{-}C_8H_{16} + 0.5c\text{-}C_6H_{12}) + (1-x)c\text{-}C_7H_{14}$	11.4067	1.3863	−3.4867
$x(0.5c\text{-}C_{10}H_{20} + 0.5c\text{-}C_6H_{12}) + (1-x)c\text{-}C_8H_{16}$	35.3082	7.7945	2.3380
$x(0.6c\text{-}C_5H_{10} + 0.4c\text{-}C_{10}H_{20}) + (1-x)c\text{-}C_7H_{14}$	183.5826	37.7464	−2.1561
	B_0	B_1	B_2
$x(0.5c\text{-}C_8H_{16}) + 0.5c\text{-}C_6H_{12}) + (1-x)c\text{-}C_7H_{14}$	−0.0092	0.0109	−0.0326
$x(0.5c\text{-}C_6H_{12} + 0.5c\text{-}C_{10}H_{20}) + (1-x)c\text{-}C_8H_{16}$	−0.0913	−0.0099	0.0529

V_m^E they are of the order of 0.002 $cm^3\ mol^{-1}$, and in x it is estimated to be less than 1×10^{-4}. The coefficients A_r and B_r are given in Table 3.

DISCUSSION

Our results show a small positive excess enthalpy and a small negative excess volume of mixing for all the mixtures. Mixtures containing the $c\text{-}C_5H_{10}$ appear to produce the greatest divergence from the congruence principle. This shows that the effect of adding a $-CH_2-$ group to $c\text{-}C_5H_{10}$ is not the same as the addition of a $-CH_2-$ group to $c\text{-}C_8H_{16}$ or $c\text{-}C_{10}H_{20}$. In general, the greater the disparity in the carbon number the greater the divergence from the congruence principle. The cycloalkane mixtures do not satisfy the congruence principle as well as the n-alkane mixtures do.

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